We've got you covered, topsides...

The predominant topside (freeboard and superstructure) coating used on U.S. Navy surface ships for the last 50 years has been haze gray silicone alkyds. These coatings are simple, single-component (1K) products that have a limitless pot-life (in a closed can) and will cure in the harsh marine environment. Unfortunately, these "user friendly" silicone alkyd paints have shown to exhibit higher levels of fading, chalking, loss of gloss, and vulnerability to rust-staining than more advanced coating systems that have entered the market over the past decade. As a result of the inherent performance limitations of silicone alkyds, sailors have historically spent a lot of their time repainting or touching-up the topsides of ships. This maintenance painting is a mundane task that can add extra weight to a ship, and if not performed in accordance with requirements, can lead to unsightly peeling of the coating.

So, the challenge faced by the Naval Sea Systems Command (NAVSEA) was to find a commercial, high-performance coating system that could shift the paradigm for the sailor from one of regularly repainting the ships to one of simply cleaning a durable, color-stable haze gray topside coating. Two-component (2K) polysiloxane coatings were identified as offering the best opportunity to shift the paradigm away from having to repeatedly repaint ship topsides. These polysiloxane products were tested on Navy ships beginning in 2005, and their enhanced color-stability, gloss retention, and cleanability versus silicone alkyds have been proven over the past 8 years. Unfortunately, these two-component products are not as "user friendly" as the single-component silicone alkyds, and will not cure properly if inadequately mixed.

NRL chemists have stepped up to the challenge to create a more "user friendly" and high performance polysiloxane topside coating. The newly designed and patented technology is a single-component polysiloxane coating that has demonstrated better color stability, hardness, solvent resistance, and adhesion than silicone alkyds when tested in the laboratory, including greater color stability than two-component polysiloxanes. The coating also has an indefinite pot-life (in a closed can) and is low in volatile organic compounds (VOCs). Preliminary results from small demonstrations aboard several Navy surface ships show that the new coating is outperforming all current qualified coatings with regard to color stability. Thus far, the new, single-component polysiloxane is proving itself as an invaluable tool for reducing the sailor painting workload, while ensuring Navy ships maintain the haze gray color over the longer term.

Single-Component Polysiloxane Coating for Navy Topsides

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Silicone alkyds have been the Navy's standard haze gray topside coating for nearly 50 years and remain the only single-component paints qualified under military specification MIL-PRF-24635 (Coating System, Weather-Resistant, Exterior Use). Although the predominant coating in the Fleet, silicone alkyd coatings are inherently limited in color and gloss retention, cure time, and exhibit limited cleanability, especially as it relates to rust staining. To address these issues, the Naval Research Laboratory (NRL) has recently designed and patented a novel single-component polysiloxane coating for Navy topsides. When tested in the laboratory, the coating has demonstrated exceptional color stability, hardness, solvent resistance, and adhesion that rivals silicone alkyds, in addition to outperforming the recently qualified two-component polysiloxane topside coatings with respect to color stability. The new coating is currently being demonstrated aboard the USS *Oak Hill* (LSD 51) and USS *Hopper* (DDG 70) surface ships. NAVSEA program sponsors are interested in transitioning the new coating to the Fleet, and NRL is working to obtain all the required performance testing, safety reviews, and chemical registrations required to field the innovative, new technology.

BACKGROUND

The U.S. Navy's predominant haze gray topside coatings are single-component silicone alkyds that are qualified under MIL-PRF-23635[1] for use on the topsides (freeboard and superstructure) of surface ships. These coatings have been in use by the Navy since the early 1960s, and were originally specified under TT-E-490[2] as semigloss coatings. These coatings have proven over the years to be "user friendly" in that they are single-component paints that have an indefinite pot-life (in a closed can), have been reformulated to maintain compliance with volatile organic compound (VOC) limits, and will cure even under the most adverse conditions. Unfortunately, these user-friendly paints have several inherent limitations, which include color fading, color shifting toward a pinkish hue with low solar absorbance (LSA) variants, chalking, loss of gloss, and limited surface hardness that makes running rust and soot staining extremely difficult to remove. In addition, peeling, cracking, and delamination of cured silicone alkyds can often result due to application over inadequately prepared surfaces. Silicone alkyd coatings have provided the Navy with decades of acceptable performance and repeated product reformulations; however, the current demands for topside coatings on Navy ships mean that evolutions of silicone alkyds have reached their end-point.

Silicone Alkyd Coatings

Silicone alkyd coatings are formulated as single-component (1K) systems (all-in-one can) because they contain unsaturated fatty acid groups that crosslink in the presence of atmospheric oxygen. The coatings do not begin to cure until they are applied to a surface and the solvent evaporates, thereby possessing essentially a limitless pot-life in a closed can. For Navy ships, silicone alkyd topside coatings are specified as a Haze Gray color (Fed. Std. 26270) with a semigloss finish, are available in a variety of volatile organic compound (VOC) levels (e.g., 340 g/L, 250 g/L), and have a service-life of approximately 6 to 12 months. Ship's Force can often be found applying silicone alkyd coatings via roller or brush for the sake of touch-up and repair during field and depot level maintenance (Fig. 1(a)), yet this mundane and non-war-related task would not be required if silicone alkyd coatings did not easily fade, discolor, peel/delaminate (Fig. 1(b)) or stain within a few months after application. A single application of silicone alkyd is specified at 2 to 5 mils dry film thickness (DFT); however, due to the constant over-coating by sailors, it is not uncommon for surface ships to possess greater than 50 mils of topside coating.

In the late 1990s, the Navy began using silicone alkyd topside coatings with low-solar-absorbing (LSA) pigments, which later became specified in MIL-PRF-24635 as Grades B and C. These pigments are incorporated to reduce the thermal loads on ships and corresponding energy required to cool the interior spaces, which can become uncomfortable for sailors on hot summer days. LSA pigments provide reflectivity of solar energy in the near-infrared (NIR) region (780 to 2500 nm), which is commonly known as the "heat region" of sunlight. Unlike non-LSA silicone alkyds that contain mainly carbon black and white to provide

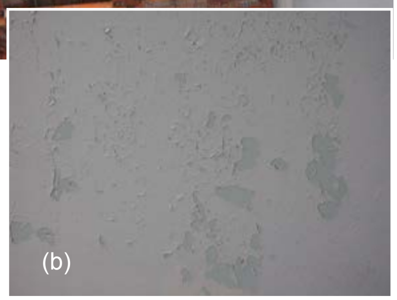

FIGURE 1
(a) Roll application of a silicone alkyd topside coating by Ship's Force, and (b) peeling/delamination of a silicone alkyd topside coating on a Navy ship.

the Haze Gray color, LSA versions yield Haze Gray by using a mixture of titanium dioxide (white), red iron oxide, yellow iron oxide, and copper phthalocyanine blue pigments. This mixture provides a reflectivity of approximately 80% in the 780 to 1200 nm range, as opposed to a mere 10% to 20% when formulated with titanium dioxide and carbon black pigments. Unfortunately, after only a short period of external exposure, many of the Grade B and C silicone alkyds change from the required Haze Gray color to a pinkish color (Fig. 2), thus deviating from the Navy's camouflage requirements.This undersirable color change results in topside over-coating by Ship's Force with more LSA silicone alkyd, thus leading to a continuous downward spiral of painting and pinking that leads to excessive coating thicknesses and additional weight to the ships.

FIGURE 2
Pinking of LSA silicone alkyd coating on the USS *San Antonio* (LPD-17).

Polysiloxane Coatings

Polysiloxane-based coatings have an inherent durability advantage over traditional organic-based materials due to the presence of silicon-oxygen bonds. The Si–O bond, which has a bond enthalpy of 110 kcal/mol, is stronger than the carbon-hydrogen (99 kcal/mol) and carbon-carbon (83 kcal/mol) bonds found in organic coatings, thereby leading to an increase in thermal stability and resistance to oxidative degradation by sunlight. Silicone alkyd coatings can contain up to 30 weight percent of silicone in the base co-polymer to improve weathering; however, this level of addition is still insufficient to overcome the poor weathering contributions from the unsaturated fatty acids groups.

Two-component (2K) polysiloxane coatings are based on materials that contain both reactive organic groups and moisture-curable alkoxysilanes in the same molecules. These coatings are often referred to as "hybrid cure coatings," where one portion of the coating is crosslinked by the ambient reaction between organic groups, such as amines and epoxies, while the other portion forms a siloxane network via moisture hydrolysis of the alkoxysilane groups and condensation of the resulting silanols. These coatings offer excellent exterior durability, hardness, chemical resistance, and direct-to-metal adhesion; however, they can suffer from photo-oxidation and yellowing due to the presence of amines in the coating. The Navy has recently qualified several commercial two-component (2K) polysiloxane coatings for topside use under MIL-PRF-24635, Type V, and all are outperforming silicon alkyd coatings in the field. Unfortunately, these polysiloxane coatings require the mixing of components before application, which can result in insufficient cure times, reduced hardness, poor adhesion, and poor appearance if Ship's Force and/or contractors do not mix the materials correctly.

Single-component (1K) polysiloxane coatings are typically based on acrylic-silane binders. These binders are manufactured via radical polymerization of gamma-methacryloxypropyltrimethoxysilane with methyl methacrylate, hexyl acrylate or other organic monomers to form linear copolymers with pendant alkoxysilane groups (Fig. 3). The copolymers are high in molecular weight and require significant quantities of solvent(s) to solubilize the large polymer chains, thus making it difficult to generate low VOC coatings. The pendant alkoxysilane groups are the only reactive functionalities on the copolymer, which enables the coating to be cured via moisture hydrolysis and condensation. Single-component coatings based on these binders are available on the commercial market from several manufacturers, although they are not without their drawbacks. For instance, these coatings are slow to hydrolyze and crosslink (cure) at room temperature when not exposed to high humidity environments, and they display poor chemical resistance when not fully cured due to the low crosslink density within the coating. These issues result because the acrylic-silane copolymers in the coating contain pendent propyltrialkoxysilane groups that are inherently slow to hydrolyze and limited in quantity when compared to non-reactive groups in the copolymer backbone. This contrasts the two-component polysiloxane coatings that contain aminopropyltrialkoxysilanes and are faster to hydrolyze. Acrylic-silane binders often possess glass transition temperatures (Tgs) above room temperature in order to provide fast dry-to-touch times (e.g., 1-3 hours) as the solvent evaporates, although this attribute should not be confused with rapid crosslinking (curing) of the binders.

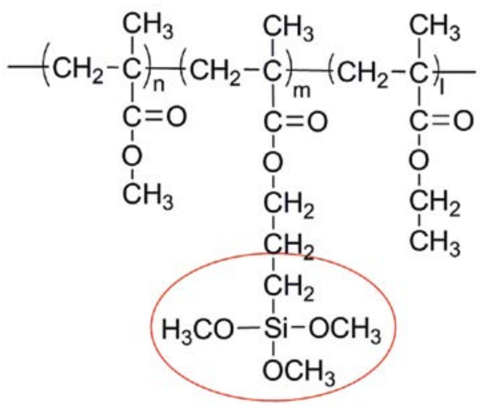

FIGURE 3
General structure of an acrylic-silane with pendent trimethoxysilane group.

A single-component polysiloxane coating that provides excellent exterior durability (color and gloss retention), low VOCs, low toxicity, good chemical resistance and adhesion, moderate cure times over a wide range of humidity, a semigloss finish, and is easy for Ship's Force to apply does not currently exist, and a solution is desperately needed for the touch-up and repair of Navy topside coatings.

Advanced Single-Component Polysiloxane Coating

The Naval Research Laboratory has recently developed a novel moisture-curable polymer for a single-component (1K) polysiloxane topside coating.[3] The technology is based on an N-substituted urea framework with terminal alkoxysilane groups (Fig. 4) and addresses the issues of slow cure times, high VOC content, and solvent resistance that are associated with commercial 1K polysiloxane coatings based on acrylic-silane copolymers. NRL's technology enables the formulation of a low VOC and Hazardous Air Pollutants (HAPS) free coating with excellent exterior durability, surface hardness, and solvent resistance, in addition to good adhesion over bare steel and epoxy primed substrates. The coating can be applied via spray, brush or roll, and most importantly, provides Ship's Force with a system that does not require the mixing of components before application.

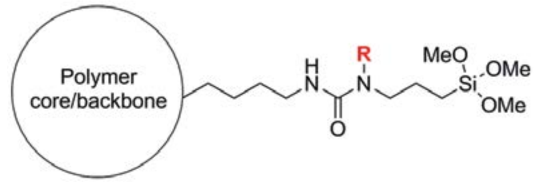

FIGURE 4
A generic structure of NRL's single-component polymer.

The polymer possesses a unique design that enables its terminal alkoxysilane groups to hydrolyze and crosslink faster than the alkoxysilanes found in acrylic-silanes. It is believed that this acceleration is due to the inclusion of specific "R" groups on nitrogen atoms of the urea linkages, which lead to accelerated hydrolysis of the terminal alkoxysilanes. This is currently under investigation at NRL. In addition, because one of the nitrogen atoms in the urea linkages contains a second substituent, the urea groups in the polymer are no longer planar, thereby providing lower intermolecular hydrogen bonding character than would otherwise be found in a traditional urea polymer. This in turn leads to a reduced viscosity for the polysiloxane polymer that requires less solvent to form a usable coating, in addition to providing for a system with greater internal flexibility.

When tested for exterior color stability using accelerated weathering instruments, NRL's 1K LSA polysiloxane outperformed qualified LSA silicone alkyds and 2K LSA polysiloxane topside coatings. As shown in Fig. 5, exposure to artificial sunlight (Xenon-Arc Weatherometer, ASTM G155) for 3000 hours resulted in a color change (ΔE) of only 0.6 for the NRL 1K polysiloxane, whereas the silicone alkyds demonstrated a pronounced color change over time. The 2K polysiloxane coating performed well, and the color change of greater than 1.0 after 3000 hours was only slightly noticeable to the eye. Exposure of the 1K polysiloxane to the more destructive UV-B radiation (ASTM G154, 313 nm bulb) for 3000 hours demonstrated a color change of less than 0.70, whereas the silicone alkyds and 2K polysiloxane began to yellow after only a few hundred hours. It should be noted that a color change of ≤1 is undetectable by the human eye.

Table 1 shows a comparison of tack-free times (ASTM D5895), surface hardness (ASTM D4366), and

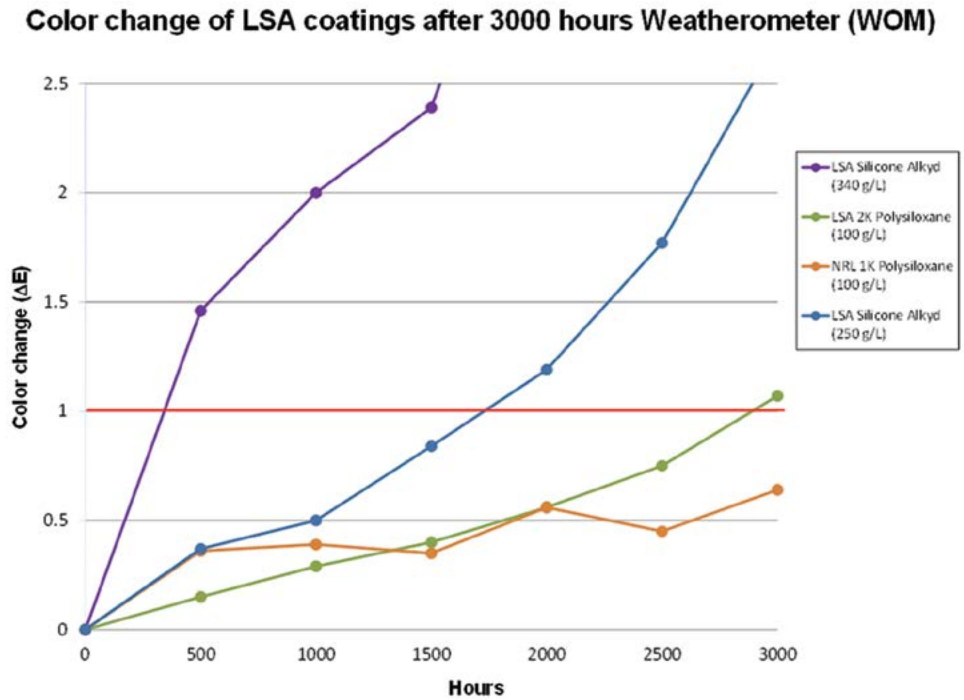

FIGURE 5
Xenon-Arc weathering comparison of NRL's 1K LSA polysiloxane coating, a Navy qualified 2K LSA polysiloxane coating, and two Navy qualified LSA silicone alkyd coatings.

TABLE 1 — Comparison of coating properties between NRL's 1K polysiloxane with various amounts of a catalyst, a commercial 1K polysiloxane (acrylic-silane based), and a Navy qualified silicone alkyd.

3 mil (75 μm) films @ 71°F, 49% R.H.

1K Coating	Tack-free times	Hardness- König Pendulum (properties after 7 days)	MEK Resistance- dbl. rubs (properties after 7 days)
NRL polysiloxane w/ 0.3% cat.	3 hrs.	76 osc.	100+ (no damage)
NRL polysiloxane w/ 0.15% cat.	3-4 hrs.	71 osc.	100+ (no damage)
NRL polysiloxane w/ no cat.	7 hrs.	21 osc.	25 (marred)
Commercial polysiloxane	1 hr.	10 osc.	8 (rubbed through)
Navy Silicone Alkyd	2 hr.	20 osc.	8 (rubbed through)

methyl ethyl ketone (MEK) solvent resistance (ASTM D4752) for NRL's 1K polysiloxane coating with various amounts of a catalyst, a commercial white 1K polysiloxane (acrylic-silane based), and a Navy qualified silicone alkyd topside coating. All coatings were applied to give 3 mil (75 μm) dry films, and were allowed to cure at ambient conditions for 7 days before being tested. As the table shows, the commercial polysiloxane and silicone alkyd have faster tack-free times than the NRL systems, which are mainly attributed to the copolymers in the coatings having glass transition temperatures (Tgs) above room temperature. However, these commercial systems are extremely slow to crosslink (cure) when compared to the NRL 1K polysiloxanes, as shown by their low surface hardness and resistance to MEK after 7 days. The NRL 1K coatings with catalysts are significantly harder and more solvent resistant, and even the coating without a catalyst had developed greater solvent resistance within the 7 day period. It is also worth noting that the NRL 1K polysiloxanes will pass a Conical Mandrel Bend (ASTM D522) test without cracking or loss of adhesion.

Several gallons of the NRL 1K polysiloxane were scaled-up by a commercial coating manufacturer, and a small test area (~100 ft^2) was used for a topside demonstration aboard the USS *Oak Hill* (LSD-51) in 2011. For the demonstration, the coating was not color-matched to Haze Gray, and thus has an appearance of a blue-gray color. The coating was inspected after 10 months of active service and remained in excellent condition with a color change (ΔE) of less than 0.25. A Haze Gray (Fed. Std. 26270) colored version was recently roll- and brush-applied by Ship's Force aboard the USS *Hopper* (DDG-70) (Fig. 6), and several additional demonstrations are planned for both Norfolk, VA- and San Diego, CA-based surface ships.

FIGURE 6
Haze Gray version of NRL's 1K polysiloxane topside coating aboard the USS *Hopper* (DDG-70).

The 1K polysiloxane coating is currently being tested and evaluated to MIL-PRF-24635, Type V and VI, Class 2, Grade B specifications under a NAVSEA program, and will transition to the Fleet if proven successful. In addition, the newly developed polymers in the coating must be registered under the EPA's Toxic Substance Control Act (TSCA) before the coating can be utilized in commercial quantities.

SUMMARY

The Naval Research Laboratory has recently developed a novel single-component (1K) polysiloxane coating for the topsides of Navy ships. The coating does not require the mixing of components before application, can be applied direct-to-metal or over an epoxy primer, and outperforms all Qualified Product Database (QPD) silicone alkyds and 2K polysiloxane coatings when tested for color stability in accelerated weathering tests. The technology is designed to give a semigloss finish; is low in VOCs; can be brushed, rolled, or sprayed; and most importantly, provides applicators, such as Ship's Force, with a topcoat that does not require the mixing of components before performing touch-up or repairs to Navy topsides. The coating is currently being demonstrated in small areas on the topsides of active Navy surface ships while also being tested and evaluated in the laboratory to MIL-PRF-24635 specifications.

ACKNOWLEDGMENTS

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[Sponsored by NAVSEA]

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[3] E.B. Iezzi, "Single-Component Coatings Having Alkoxysilane-Terminated N-Substituted Urea Resins." U.S. Patent 8,133,964, March 13, 2012.

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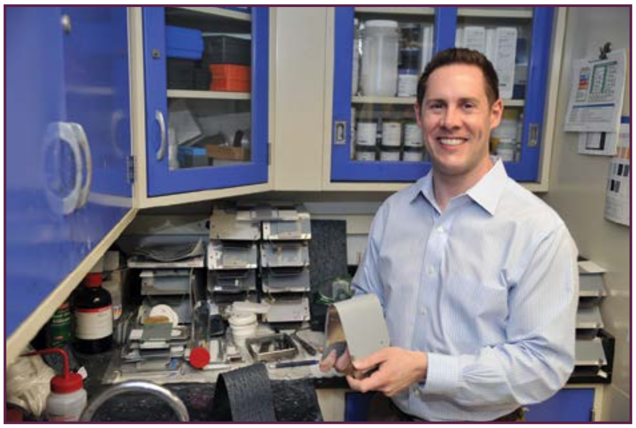
THE AUTHORS



ERICK IEZZI obtained his Ph.D. in organic chemistry from Virginia Tech in 2003, where he was an ACS Division of Organic Chemistry Graduate Fellow. This was followed by a National Institutes of Health (NIH) Postdoctoral Fellowship at the University of Pittsburgh from 2004 to 2006, where he worked on the multistep total synthesis of diazonamide A, a natural anticancer compound. He then joined PPG Industries in 2006, where he worked on developing UV and moisture-curable coatings for the Automotive Refinish and Aerospace Groups. In 2008, he moved to the Naval Research Laboratory as a contractor, where he designed and formulated ship-based coatings for the Center for Corrosion Science and Engineering (Code 6130). In 2012, Dr. Iezzi formally joined NRL as a research chemist, where he manages several programs, synthesizes new materials (e.g., polymers and small molecules) and designs novel coating systems for U.S. Navy ships, submarines, aircraft, and Marine Corps vehicles, collaborates with coating manufacturers to scale-up technologies, and provides application support during product demonstrations. He also advises coating manufactures on ways to improve current and future military specified (MIL-SPEC) coatings. Erick has developed a siloxane-based nonskid coating, two-component topside coatings, and a novel single-component topside coating that are all currently being demonstrated on several active Navy surface ships.

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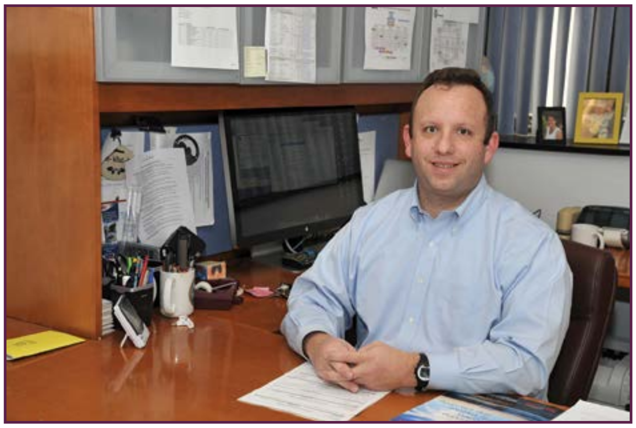
PAUL SLEBODNICK is currently employed at the Naval Research Laboratory in Washington, DC, Center for Corrosion Science and Engineering, under the Marine Engineering Section. Mr. Slebodnick currently leads research programs in developing technologies for the U.S. Naval Fleet that produce maintenance reductions and reduce Ship's Force workload. Mr. Slebodnick is responsible for demonstrating new technologies aboard Fleet combatants to determine readiness with in-service evaluation of the technologies prior to transitioning to the Fleet. Many of these innovative technologies are developed at NRL and have been demonstrated aboard ships and submarines with documented maintenance reductions. Mr. Slebodnick is also an Engineering Manager for Research and Development of Tank Coatings for the Naval Sea Systems Command, Technical Warrant Holder, SEA-05 in Washington, DC.



TED LEMIEUX is currently the Director of the Center for Corrosion Science and Engineering at NRL in Washington, DC. Mr. Lemieux currently leads and directs a diverse research portfolio in marine corrosion, coatings, cathodic protection, environmental effects on materials, fouling control, condition-based maintenance, and material science in general. Mr. Lemieux is also an Engineering Agent for both Corrosion Control and Cathodic Protection for the Naval Sea Systems Command.

JAMES TAGERT graduated from the University of Maryland, College Park, in 2004 with a B.S. in mechanical engineering. He received his engineer-in-training certificate from the state of Maryland in 2006 and since graduation has worked in the materials engineering field. He is a member of both the American Society of Naval Engineers and National Association of Corrosion Engineers and participates regularly with both groups, informing them of research ongoing at the Lab. Jimmy has worked at NRL since 2008, supporting the U.S. Navy in research and engineering programs related to materials science with an emphasis on the development and transition of advanced topside and nonskid coating systems for the Fleet. He formally joined NRL in December 2012.

JAMES MARTIN has been with the Naval Research Laboratory for 13 years. He is the Section Head of the Marine Coatings Technology and Systems group. He is responsible for introducing coatings technology to the Fleet through development, testing, and demonstrations. Nearly all aspects of coatings transition are addressed, including surface preparation and application processes and equipment, specifications, analytical and failure analysis, testing and evaluation for qualification and new chemistry development, novel removal methods, and field support. He has been active in addressing Fleet concerns from both maintenance and new construction with respects to coatings. James continues to introduce new technology that will help to reduce the lifecycle ownership costs of today's Fleet.